ALCOHOL SYNTHESIS OVER Fe/Cu/ZnO CATALYSTS

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INTRODUCTION

In the attempt to produce higher molecular weight oxygenated compounds from synthesis gas (H_2 + CO) for utilization as fuels and intermediate chemicals, an approach to catalytically forming higher alcohols is to combine an alkyl-forming agent with a methanol synthesis catalyst. It is well-known that copper-based catalysts are very selective for the synthesis of methanol (1-3). On the other hand, cobalt- and iron-based catalysts promote the Fischer-Tropsch synthesis (4,5) of hydrocarbons. The Fischer-Tropsch process converts synthesis gas to a mixture of predominantly linear alkanes and alkenes rather non-selectively but in such a manner that the product distribution with respect to carbon chain length displays a recognizable pattern (6-8), commonly referred to as the Schulz-Flory distribution (9,10). This distribution arises from the stepwise catalytic polymerization and hydrogenation of CO by processes whose reaction mechanisms have not been fully established (11-13).

Utilizing mixed copper/cobalt catalysts has led to enhanced selectivities for the synthesis of higher alcohols (14-19). However, the quantity of hydrocarbons formed were greater than the quantity of higher alcohols formed (18,19), methane was the dominant product (15,16), or methanol was the most selectively formed product (14,17,18). It appears that the copper/cobalt catalysts that contain small amounts of cobalt (<8 wt%) are principally methanol synthesis catalysts in which the cobalt has suppressed the catalytic activity while shifting the selectivity toward higher molecular weight products (19). The distribution of products, which are linear, indicates that they are formed by a Fischer-Tropsch mechanism.

Iron-based Fischer-Tropsch catalysts are usually promoted with copper, e.g. 20% Cu relative to Fe (20-23), where the copper increases the activity of the catalysts via its redox properties during the preparation of the catalysts (20,22). Oxygenates are often observed as products over these catalysts, but the yields of these products are inversely proportional to the reactant stream space velocity, e.g. more oxygenates are formed at lower gas hourly space velocities (GHSV) (21). The linear products that are synthesized over these catalyst follow the Schulz-Flory distribution.

The present work has utilized a well-characterized Cu/ZnO = 30/70 mol% methanol synthesis catalyst (2,24-27) into which small amounts of iron have been introduced. It is shown that the incorporation of the latter alkyl-forming agent caused the production of higher molecular weight compounds, both paraffins and olefins, as well as alcohols.

EXPERIMENTAL

The Fe/Cu/ZnO catalysts were coprecipitated from heated nitrate solution by sodium carbonate, calcined, pelletized, and reduced with H_2/N_2 = 2/98 vol% at 250°C according to a procedure previously described in detail for the binary Cu/ZnO catalysts (2,25). A schematic of the catalytic reactor system has been presented (2), but a high pressure unit for pumping liquids into the synthesis gas stream at a reactor pressure of 75 atm has been added at the top of the reactor preheater sec-

tion (28). The exit gas was reduced to ambient pressure and was sampled approximate-
every hr using a heated automatic sampling valve and analyzed using an on-line
Hewlett-Packard 5730A gas chromatograph coupled with a H-P Model 3388A Integrator/
Controller. Condensables (at 0°C) were collected and further analyzed by direct liq-
uid injection into the H-P GC and a Finnigan 4021 GC/MS/Nova system. The analyses
resulted in less than 2% error in the carbon atom balance.

The catalysts were characterized by BET surface area determination using argon
and by electron microscopy using a Philips 400T electron microscope fitted with a
STEM unit and an X-ray energy dispersive spectrometer.

RESULTS

The influence of iron concentration on the catalytic activity of the Fe/Cu/ZnO
catalysts was determined for the usual testing conditions employed for methanol syn-
thesis catalysts. The results are given in Table 1, and it is evident that the ac-
tivities of the catalysts decrease with increasing iron content. These conversions
can be compared with the 55 ± 5% carbon conversion observed with the undoped Cu/ZnO =
30/70 methanol catalyst (26). The catalyst containing the lowest iron content pro-
duced predominantly methanol, while the catalyst containing 9.0 mol% iron produced an
appreciable quantity of waxes. Therefore, the Fe/Cu/ZnO = 1.2/31.8/67.0 catalyst was
chosen for further study.

In examining the effect of CO_2 concentration in the synthesis gas on the activ-
ity and selectivity of the catalyst, it was observed that the maximum conversion to
products (12.0 mol%) and the greatest selectivity to C_2-C_7 hydrocarbons (60.7 C atom
%) occurred with a H_2/CO/CO_2 = 70/28/2 vol% synthesis gas. However, the highest se-
lectivities toward methanol and methane were produced by the H_2/CO/CO_2 = 70/24/6 vol%
synthesis gas (see Table 1). On the other hand, the highest selectivity toward the
C_2-C_5 alcohols (17.1%) was achieved with CO_2-free H_2/CO = 70/30 synthesis gas to
yield a C_2-C_5/C_1 alcohol molar ratio of 0.61.

Using the binary H_2/CO synthesis gas, the effect of the partial pressure of the
reactants on the higher alcohol synthesis was investigated. The results are pre-
sented in Table 2, and it is evident that as the H_2/CO ratio decreased, the % carbon
conversion to products also decreased. However, the water gas shift reaction became
more efficient at the same time so that the selectivity of CO conversion to CO_2 in-
creased as the H_2/CO ratio decreased. As the latter ratio decreased, the selectiv-
ity toward the higher alcohols relative to methanol increased. Analyses of the con-
densable liquids collected from the reactions with the low H_2/CO ratio synthesis
gases showed that traces of 2-methyl-1-propanol and 2-methyl-1-butanol were present.
It was estimated that these trace compounds were each less than 5 wt% of the total
C_4 and C_5 alcohol product.

In studying the effects of the synthesis gas feed rate on alcohol synthesis,
the inlet GHSV was varied in four steps from 2500 to 6250 hr^{-1} (contact time = 1.44
to 0.58 sec, respectively) with the H_2/CO = 50/50 gas mixture. As the contact time
increased, the carbon conversion to alcohols and hydrocarbons increased in a direct-
ly proportional manner. The carbon atom ratio of higher alcohols to methanol re-
mained relatively constant at 2.1 ± 0.1, while the alcohol/hydrocarbon molar ratio
decreased with increasing contact time. Thus, longer contact times favored hydro-
carbon synthesis, while shorter contact times shifted the selectivity towards the
alcohols. This indicates that both alcohols and hydrocarbons are primary products.

This was further supported by injecting liquid isopropylamine into the inlet
synthesis gas stream under the experimental conditions given in Table 3. The small
quantity of isopropylamine pumped into the system had little effect on the carbon
conversion. However, the production of alcohols was completely suppressed, while
the synthesis of hydrocarbons was only partially inhibited, particularly the forma-

TABLE 1

Conversion of $H_2/CO/CO_2$ = 70/24/6 vol% Synthesis Gas to Products at 250°C, 75 atm, and GHSV = 5000 hr^{-1} over Fe/Cu/ZnO Catalysts

Fe/Cu/Zn (mol%)	0.3/32.1/67.6	1.2/31.8/67.0	9.0/31.4/59.6
Catalyst Charge (g)	2.4547	2.4556	2.6971
Total Conversion			
CO + CO_2 (mol%)	23.1	10.6	8.3
(mol/kg cat/hr)	17.0	8.0	6.3
Selectivity (C atom%)			
Methanol	95.2	16.0	5.1
Ethanol	0.4	4.2	7.8
1-Propanol	0.0	2.4	2.8
2-Propanol	0.0	0.2	0.2
1-Butanol	0.0	1.4	2.2
1-Pentanol	0.0	0.7	1.2
Methane	1.4	24.3	17.9
Ethane	0.7	9.0	10.2
Ethylene	0.0	1.0	1.0
Propane	0.1	12.4	7.3
Propylene	0.0	1.0	7.6
C_4–C_7 Hydrocarbons	2.2	23.3	24.5
C_5^+ Alcohols and			
C_8^+ Hydrocarbons	0.0	4.1	11.2
Group Mole Ratios			
C_2–C_5 Alcohols/Methanol	0.002	0.22	1.12
C_1–C_5 Alcohols/C_1–C_7			
Hydrocarbons	38.9	0.51	0.31
C_2–C_3 Olefins/C_2–C_3			
Paraffins	0.0	0.10	0.47
Yields (g/kg cat/hr)			
Methanol	518	41.0	10.3
C_2–C_5 Alcohols	1.6	15.6	18.3

tion of methane and ethane. Thus, the hydrocarbon distribution was shifted slightly toward longer chain molecules and, as indicated in Table 3, from paraffins to olefins. It is evident from the data for the amines that the injected isopropylamine principally trapped methyl and ethyl groups.

A reduced Fe/Cu/ZnO = 1.2/31.8/67.0 catalyst was examined by electron microscopy after being ultrasonically dispersed from an ethanol suspension onto a carbon-coated titanium grid. Metallic copper crystallites, predominantly with a diameter of about 5.0 nm, were supported on the ZnO matrix. Electron diffraction showed that Cu ($\bar{1}11$) planes. Using a 5 nm electron probe, energy dispersive X-ray analysis of the ZnO phase indicated that it contained about 15% Cu and 0.8% Fe. A few bimetallic Fe-Cu particles were observed that contained more iron than copper. However, in general the iron was homogeneously dispersed over the catalyst.

Analysis of a tested catalyst by Auger spectroscopy indicated that the atomic composition of the surface was Cu/Zn/O/C = 15.0/9.9/6.2/68.9 %. No Fe was detected by Auger or X-ray photoelectron spectroscopy. Thus, it appears that carbon covered the iron and most of the ZnO surface, but much of the copper phase was left exposed. The BET surface area of the used catalyst, as removed from the reactor under a

TABLE 2

Reactant Concentration Effects on Alcohol Synthesis over the 1.2% Iron Catalyst at 250°C, 75 atm, 5000 hr^{-1} and $H_2/CO/CO_2$ = 30/70/0 to 70/30/0. Catalyst Charge = 2.4524g.

$H_2/CO/CO_2$ (vol%)	30/70/0	40/60/0	50/50/0	60/40/0	70/30/0
Conversion					
CO (mol%)	1.5	2.8	4.3	6.5	8.2
(mol/kg cat/hr)	2.7	4.1	5.4	6.5	6.1
Yields (g/kg cat/hr)					
Methanol	4.1	9.2	15.1	18.2	17.7
Ethanol	3.2	6.5	9.4	10.6	9.0
1-Propanol	1.8	3.9	5.4	5.6	4.9
2-Propanol	0.2	0.4	0.5	0.4	0.4
1-Butanol	0.9	2.0	2.9	2.9	2.7
1-Pentanol	0.4	1.0	1.5	1.5	1.3
Selectivity (C atom%)					
Carbon Dioxide	41.5	30.5	23.9	19.6	16.8
Methanol	4.8	6.9	8.7	8.8	8.9
C_2-C_5 Alcohols	11.4	15.9	17.4	15.4	14.2
C_1-C_7 Hydrocarbons	42.3	46.7	50.0	56.2	60.1

nitrogen atmosphere, was 0.4 m^2/g, and this contrasts with the surface area of 37-40 m^2/g for tested binary Cu/ZnO = 30/70 catalysts (25,26). After washing the tested ternary catalyst with cyclohexane, the surface area was found to be 15 m^2/g.

DISCUSSION

The composition of the synthesis gas mixture has a pronounced effect on the selectivity observed over the Fe/Cu/ZnO catalyst. The presence of CO_2 in the synthesis gas tends to favor the formation of low molecular weight products, i.e. methanol and methane. When CO_2 is removed from the reactant stream, carbon chain growth is promoted, apparently due to exposure of sites active in the transfer of alkyl groups. In the absence of CO_2, the percentage of CO converted to carbon dioxide, alcohols, and hydrocarbons increased as the H_2/CO ratio was increased from 0.43 to 2.33. Similar behavior has been observed with other iron catalysts, for which the rate of synthesis increased as the hydrogen content of the feed increased (6).

The carbon chain growth reactions that occurred over these iron-containing catalysts can be treated as a polymerization process in which the molecular weight distribution of products is determined by the chain propagation and chain transfer steps. The Schulz-Flory molecular weight distribution can be derived to give the following equation:

$$N_x = N_0(1-\alpha)^2\alpha^{x-1}, \qquad\qquad 1)$$

where N_x is the total number of molecules containing x carbon atoms, N_0 is the total number of monomer units ($-CH_2-$) in the system, and α is the probability of chain growth (28). Equatiion 1 can be expressed in logarithmic form as

TABLE 3

Effects of Isopropylamine on Product Distributions over a 1.2% Fe
Containing Cu/ZnO Catalyst at 235°C, 75 atm, 5000 hr^{-1}, and $H_2/CO/CO_2$ =
70/30/0 vol%. Catalyst Charge = 2.414 g. (R = isopropyl).

Isopropylamine in Feed (µl/min)	0	20
$H_2/CO/RNH_2$ (molar ratio)	2.33/1.00/0	2.33/1.00/0.08
CO Conversion (mol%)	4.45	4.38
(mol/kg/hr)	3.4	3.3
Products ($\times 10^{+4}$ mol/hr)		
C_1-C_5 Alcohols	7.03	0
C_1-C_7 Hydrocarbons	38.43	23.01
Amines:		
$R-NH-CH_3$	0	1.01
$R-N-(CH_3)_2$	0	1.34
$R-NH-C_2H_5$	0	0.70
$R-N-(CH_3,C_2H_5)$	0	7.71
$R-N-(C_2H_5)_2$	0	0.35
$R-NH-(n-C_3H_7)$	0	0.38
Certain Molar Ratios		
Alcohols/Hydrocarbons	0.2	0
Olefins/Paraffins	0.1	1.4

$$\log (N_x/N_o) = \log [(1-\alpha)^2/\alpha] + x\log\alpha. \qquad 2)$$

If the graphical representation of $\log (N_x/N_o)$ vs x gives a straight line, and the
values of α determined from the intercept and the slope are in good agreement, then
the molecular weight distribution follows the Schulz-Flory law.

Figure 1 demonstrates that both the alcohols and the hydrocarbons produced over
the Fe/Cu/ZnO catalyst follow the Schulz-Flory law. The propagation constant (α) is
0.32 for the alcohols, while it is equal to 0.55 for the hydrocarbons. This dis-
tinct difference in α values again suggests that the alcohols and the hydrocarbons
are formed by different pathways over this catalyst. In the absence of CO_2 and at a
lower temperature of 235°C, the distributions for alcohols and hydrocarbons yield α
values of 0.47 and 0.53, respectively. Upon addition of isopropylamine to the reac-
tor feed gas (Table 3), the production of alcohols was stopped, while the hydrocar-
bon distribution was shifted toward longer chain products to give $\alpha = 0.58$. The
distribution of alkyl groups on the product amines (excluding the isopropyl group)
yielded a non-linear plot, showing that the formation of these alkyl groups do not
follow the Schulz-Flory distribution. This indicates that the amines primarily at-
tack the alcohol precursor. If the amines had reacted with the alcohols after they
formed, the Schulz-Flory distribution of the alkyl groups would have produced the
same distribution as that of the alcohols with $\alpha = 0.47$.

The yield of C_2 substituted amines lies above the expected value found for the
alcohol distribution, while the quantities of C_1 and C_3 alkylated amines fall below
the expected values. This could be due to a methyl transfer reaction, as reported
previously (29), to form a C_2 oxygenated species that is readily attacked by the
amine. The results of the present amine trapping experiments are in contrast to
those obtained with ammonia and synthesis gas over other iron catalysts (30). In
the latter work, exclusively primary amines were formed that obeyed the Schulz-Flory
distribution to give $\alpha = 0.69$. It was proposed that ammonia attacked ($-CH_x$) inter-

mediates. However, in the presence work, it is evident that the amines reacted with the oxygenated intermediates and that the hydrocarbon intermediate was left essentially undisturbed.

CONCLUSIONS

While a complete mechanistic reaction scheme has not been verified for this catalyst system, the following conclusions have been deduced from the experimental data:

(a) both alcohols and hydrocarbons are primary products formed over the Fe/Cu/ZnO catalysts,

(b) two polymerization processes are indicated, one with short carbon chain length for alcohols and one with the usual chain length for hydrocarbons,

(c) the alcohols are formed by interaction of methanol precursors and iron-bound intermediates, with the methanol precursor behaving as a monomer in the alcohol synthesis,

(d) the optimum catalysts for the synthesis of C_2-C_5 alcohols contain small amounts of iron (~1%), which is homogeneously dispersed throughout the catalyst, and

(e) hydrocarbon growth appears to occur very actively over Fe-Cu intermetallic particles.

ACKNOWLEDGMENT

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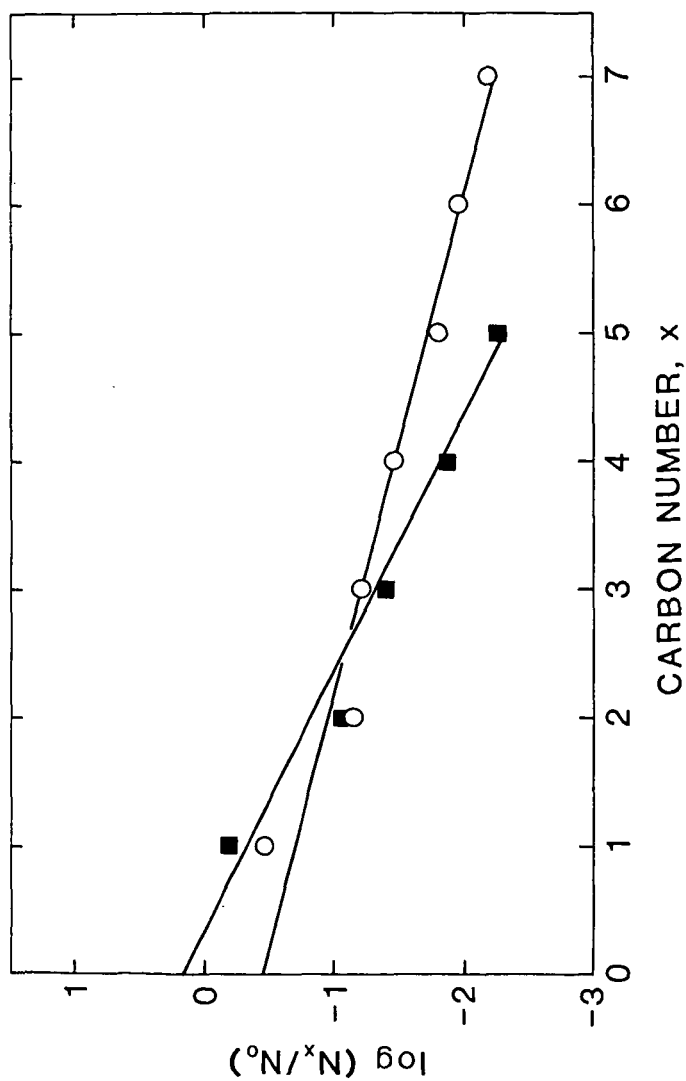30. Olivé, H. and Olivé, S., Angew. Chem., Int. Ed. Engl. (1976), 15, 136.

FIGURE 1. The Schulz-Flory Distribution of Alcohols (■) and Hydrocarbons (O) Produced over the Fe/Cu/ZnO = 1.2/31.8/67.0 mol% Catalyst from $H_2/CO/CO_2$ = 70/24/6 vol% Synthesis Gas at 75 atm, GHSV = 5000 hr^{-1}, and 250°C.